Copper(II) promoted hydrolysis of 2,4,6-tris(2-pyridyl)-1,3,5-triazine: Synthesis, characterization and biological activities of the hydrolytic products


Department of Chemistry, APS University, Rewa 486 003, MP, India

Email: rnp64@ymail.com

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The hydrolysis of 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) yield the compounds bis(2-pyridylcarbonyl)amide and 2-picolinamide. From these hydrolytic products, two copper(II) complexes viz. [Cu(IDA)(2-pa)].2H2O (1) and [Cu(bpca)(H2O)2]NO3.2H2O (2) [where IDA = iminodiacetic acid, 2-pa = 2-picolinamide and bpca = bis(2-pyridyl-carbonyl)amido] have been isolated and structurally characterized by single crystal X-ray diffraction studies. Both complexes belong to the triclinic crystal system having space group P-1. Complex (2) shows significant hydrogen bonding and non-covalent π…π stacking interactions. In complex (2), Bifurcated (three centered) hydrogen bonds have been detected. The electron paramagnetic mononuclear copper(II) complexes display X-band epr spectra in 100% DMSO at 77 K giving $g_{\parallel} > g_{\perp} > 2.0023$, indicating $d_{x^2-y^2}$ ground state in a square pyramidal geometry. In-vitro antibacterial study has been assayed against some selected microorganisms using agar disc diffusion method. The DNA cleavage activities of both complexes are also investigated by gel electrophoresis using pBR 322 DNA.

Keywords: Coordination chemistry, X-ray crystal structure, Bifurcated hydrogen bonding, Hydrogen bonding, EPR spectroscopy, DNA cleavage, Copper, Triazines

In recent years, 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) has been of current interest due to its use as a spacer for designing multinuclear metal complexes or coordination polymers. The possibility of this ligand to coordinate to metal through the terpyridine or bipyridine like moieties and using both sites simultaneously has been well characterized. Learner and Lippard reported that copper(II) ion promotes the hydrolysis of tptz molecule to form (2-pyridylcarbonyl)amidocopper(II) and free 2-picolinamide. Gil and Gillard reported that hydrolytic reaction to yield the carboximidate ligand could be viewed as taking place via nucleophilic attack at the triazine ring by OH or H2O.

The objective of the present work is to synthesize, characterize and explore the biological activities of the hydrolytic products. Observations indicate the presence of three centered hydrogen bondings (HBs). Bifurcated (or three centered) hydrogen bonds have been used to explain a large number of biological structures and are commonly used by biochemists and biologists to account for certain interactions in biological systems. This is in agreement with the fact that bifurcated hydrogen bonds occurs frequently in the crystal structure of zwitter ionic amino acids (~70%) as shown by Jeffery. Keeping this in view we have synthesized two copper(II) complexes containing hydrolytic product of tptz molecule. Herein, we report the synthesis, structure, spectral, electrochemical studies, superoxide dismutase, DNA cleavage and antibacterial activities of two new copper(II) complexes, viz., [Cu(IDA) (2-pa)].2H2O (1) and [Cu(bpca)(H2O)2]NO3.2H2O (2). Complex (2) shows the existence of three centered hydrogen bondings. The hydrolytic products of tptz are present in both the complexes.

Materials and Methods

All the chemicals used were synthetic grade, purchased from the commercial sources and used without further purification.

The elemental analysis of the complexes was carried out on an Elementar Vario ELIII Carlo Erba 1108 Elemental analyzer. UV-vis spectra of the complexes were recorded at room temperature on a Shimadzu 1601 double beam UV-visible spectrophotometer. IR spectra were recorded on a Perkin-Elmer 783 spectrophotometer in KBr medium. Electron paramagnetic resonance (epr) spectra were recorded with a Varian E-line Century Series epr
spectrometer equipped with a dual cavity and operating at X-band of 100 kHz modulation frequency. Tetracyanoethylene was used as field marker (g = 2.00277).

Synthesis of \([\text{Cu(IDA)}(2-pa)]\cdot 2\text{H}_2\text{O} \ (1)\)

In a hot aqueous suspension (20 mL) of basic copper carbonate (0.5 mmol, 0.110 g), iminodiacetic acid (1 mmol, 0.133 g) was added and when the solution became clear blue, tptz solution (1 mmol, 0.312 g) in methanol (20 mL) was added and stirred for 2 hours at 50 °C. The resulting blue colored solution was filtered off and kept under room temperature. After one week, blue black shaped crystals were collected by filtration and stored in CaCl\(_2\) desiccator. Anal. (%): Calc. for C\(_{10}\)H\(_{13}\)CuN\(_3\)O\(_7\) (1) C, 34.24; H, 3.74; N, 11.98. Found: C, 34.51; H, 3.92; N, 12.18. IR (KBr, cm\(^{-1}\)): 3433, 3261, 3034, 1710, 1618, 1451, 1384, 1350, 1259, 1152, 1097, 1034, 977, 931, 824, 793, 761, 706, 640, 552, 497, 424.

Synthesis of \([\text{Cu(bpca)}(\text{H}_2\text{O})_2]\cdot \text{NO}_3\cdot 2\text{H}_2\text{O} \ (2)\)

In an aqueous solution (20 mL) of copper nitrate (1 mmol, 0.241 g), tptz (1 mmol, 0.312 g) was added and stirred for 3 hours at 60 °C. The resulting blue colored solution was filtered off and kept at room temperature. After one week, dark blue, block shaped crystals were collected by filtration and stored in CaCl\(_2\) desiccator. Anal. (%): Calc. for C\(_{12}\)H\(_{16}\)CuN\(_4\)O\(_9\) (2) C, 34.01; H, 3.81; N, 13.22. Found: C, 34.22; H, 3.65; N, 12.93. IR (KBr, cm\(^{-1}\)): 3460, 3252, 3091, 3036, 1717, 1638, 1603, 1439, 1375, 1288, 1156, 1097, 1034, 914, 830, 761, 699, 548, 491, 460, 420.

Single crystal X-ray structure determination

Single crystal X-ray data were collected on a CCD detector based diffractometer, (SMART APEX) from Bruker-Nonius Axs and CrysAlisPro, Oxford diffractometer using graphite monochromatized Mo-K\(_\alpha\) (\(\lambda = 0.71073\)Å). The diffraction data was solved using SIR-92\(^{16}\) with GUI control and structure was refined by SHELXL-97\(^{17}\) refinement of \(F^2\) against all reflections. Non-hydrogen atoms were refined anisotropically. All hydrogen atoms were geometrically fixed and allowed to refine using a riding model. Molecular graphics were generated using different software such as ORTEP-3v2 for WINDOWS\(^{18}\), PLATON and Mercury\(^{19}\).

DNA cleavage

DNA cleavage experiments were performed by agarose gel electrophoresis method\(^{20}\). The efficiency of DNA cleavage was measured by determining the ability of the complexes to form open circular (OC) and nicked circular (NC) DNA from its super coiled (SC) form. The DMSO solution (1×10\(^{-3}\)M) containing metal complexes (5 µL, 250 µM) were taken in a clean Eppendorff tube and 1 µg of pBR 322 DNA was added. The contents were incubated for 30 min at 30 °C and loaded on 0.8% agarose gel after mixing 3 µL of loading buffer (0.25% bromophenol blue + 0.25% xylene cyanol + 30% glycerol in sterilized distilled water). The electrophoresis was performed at constant voltage (75 V) until the bromophenol blue reached upto 3/4 length of the gel. Further, the gel was stained for 10 min by immersing it in ethidium bromide solution (5 µg/mL of water) and then de-stained for 10 min by keeping it in sterile distilled water. The plasmid bands were visualized by photographing the gel under a UV transilluminator (gel documentation assembly). The reactions were carried out under oxidative and/or hydrolytic condition.

Results and Discussion

The triazine, tptz, was used in the synthesis of both complexes as a primary ligand and conventional solution method was adopted. Copper(II) ion promotes hydrolysis of tptz in aqueous solution yielding the anionic bis(2-pyridylcarbonyl)amido and 2-picolinamide (Scheme 1). The complexes were readily formed by the reaction of ligands and copper(II) salt. It was observed and confirmed by X-ray diffraction that tptz was hydrolyzed in both reactions. The complex (1) was obtained when a hot aqueous solution of basic copper carbonate and IDA...
was interacted with tptz. Both complexes gave satisfactory elemental and IR spectra data, which were further characterized by single crystal X-ray diffraction.

**Single crystal X-ray structure**

The crystal structures of [Cu(IDA)(2-pa)2H2O (1)] and [Cu(bpca)(H2O)2]NO3.2H2O (2) belong to triclinic crystal system having space group P-1. Crystal data and structure refinement parameters are listed in Table 1.

An ORTEP view of the complex (1) is shown in Fig. 1. Selected bond distances and angles are given in the Table 2. The basal plane is formed by N(1), N(2), O(1) and O(4), which are coordinated to copper(II) [Cu(1)-N(1) 1.993(3), Cu(1)-N(2) 2.019(3), Cu(1)-O(1) 1.974(3) and Cu(1)-O(4)]

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**Table 1 – Crystal data and structure refinement parameters for complexes (1) and (2)**

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<thead>
<tr>
<th>Parameter</th>
<th>Complex (1) C20H13CuN3O7</th>
<th>Complex (2) C21H16CuN4O9</th>
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<tr>
<td>Empirical formula</td>
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<td>C21H16CuN4O9</td>
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<td>Formula weight</td>
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<td>423.84</td>
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<td>Temperature (K)</td>
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<td>293(2)</td>
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<td>Wavelength (Å)</td>
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<td>Triclinic</td>
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<td>P-1</td>
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<td></td>
<td>b (Å) 0.3502(9)</td>
<td>10.1890(10)</td>
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<td></td>
<td>c (Å) 15.7437(15)</td>
<td>12.0166(11)</td>
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<td></td>
<td>α(°) 79.197(8)</td>
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<td>β(°) 74.875(8)</td>
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<td>434</td>
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<td>0.41 x 0.36 x 0.32</td>
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<td>1.71 to 25.00</td>
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<td>Limiting indices</td>
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<td>-8&lt;=h&lt;=8, -12&lt;=k&lt;=12, -14&lt;=l&lt;=14</td>
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<td>7963/ 2893 [R(int) = 0.0325]</td>
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<td>Completeness to θ = 25.00°</td>
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<td>99.7%</td>
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<td>Semi-empirical from equivalents</td>
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<td>Full-matrix least-squares on F^2</td>
<td>Full-matrix least-squares on F^2</td>
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<td>Data/ restraints/ parameters</td>
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<td>2893/ 263</td>
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<td>Goodness-of-fit on F²</td>
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<td>Final R indices [I &gt;2σ(I)]</td>
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<td>R1 = 0.0331, wR2 = 0.0775</td>
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<td>R indices (all data)</td>
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<td>R1 = 0.0351, wR2 = 0.0789</td>
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<td>Largest diff. peak and hole (e Å⁻³)</td>
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<td>0.329 and –0.371</td>
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**Fig. 1 – ORTEP view of [Cu(IDA)(2-pa)].2H2O (1) showing the numbering scheme.**
The axial position is occupied by O(6) with Cu-O distance of 2.249(2) Å. Iminodiacetic acid is coordinated to copper(II) via two carboxylato oxygen and one nitrogen atom, while 2-picolinamide ligand is coordinated via the nitrogen atom N(1) of the pyridine ring and the oxygen atom of amide group with distance of 1.993(3) and 1.974 Å respectively. Two unsymmetrical molecules of complex (1) are present in the cell. The distance between two copper (II) centres is 4.06 Å in complex (1).

An ORTEP view of [Cu(bpca)(H₂O)₂]NO₃·2H₂O (2) is shown in Fig. 2. Bis (2-pyridylcarbonyl) amido ligand is coordinating to copper(II) via three nitrogen donor atoms. This ligand is formed by the hydrolysis of tptz during the reaction. The three Cu-N bond lengths are quite similar [Cu(1)-N(1) 1.993(2), Cu(1)-N(3) 1.935(2) and Cu(1)-N(111) 1.993(2) Å]. The geometry around the copper(II) can be described as distorted square pyramidal. Two water molecules [O(1) and O(2)] are coordinating to central atom and O(2) occupies the axial position.

Both complexes are five coordinated with a distorted square pyramidal geometry as indicated by

<table>
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<th>Complex (1)</th>
<th>Bond Lengths (Å)</th>
<th>Angles (°)</th>
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<tr>
<td>N(1)-Cu(1)</td>
<td>1.993(3)</td>
<td>O(6)-Cu(1)</td>
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<td>N(2)-Cu(1)</td>
<td>1.995(3)</td>
<td>N(111)-Cu(1)</td>
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<td>N(3)-Cu(2)</td>
<td>1.995(3)</td>
<td>O(10)-Cu(2)</td>
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<td>N(4)-Cu(2)</td>
<td>2.009(3)</td>
<td>O(12)-Cu(2)</td>
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<td>O(1)-Cu(1)</td>
<td>1.974(3)</td>
<td>O(4)-Cu(1)</td>
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<td>C(5)-N(1)-Cu(1)</td>
<td>126.6(2)</td>
<td>O(4)-Cu(1)-N(2)</td>
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<td>C(1)-N(1)-Cu(1)</td>
<td>114.0(2)</td>
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<td>C(8)-N(2)-Cu(1)</td>
<td>107.7(2)</td>
<td>N(1)-Cu(1)-N(2)</td>
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<td>113.8(2)</td>
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structural indexing parameter, $\tau$, which measures the degree of trigonality of pentacoordinated geometry. The trigonally index $\tau$ is calculated using the equation $\tau = (\beta - \alpha)/60^{21}$, where $\alpha$ and $\beta$ are the largest coordination angles (for perfect square pyramidal and trigonal bipyramidal geometries the value of $\tau$ are zero and unity, respectively). The value of $\tau$ is 0.241 and 0.09 for (1) and (2) respectively, which indicates distortion in square pyramidal geometry. Comparison of $\tau$ values shows that complex (1) is more distorted than complex (2).

Hydrogen bond interaction data for both complexes show that four molecules are present in the unit cell of complex (1) (Supplementary Data, Table S1). Hydrogen bond are formed between adjacent molecules by the uncoordinated water molecules. N-H…O and O-H…O type inter molecular hydrogen bonds are present, which stabilize the structure of the molecules. In complex (2), the nature of bifurcated (or three-centered) hydrogen bonds (Fig. 3) have been investigated along with normal hydrogen bonds. Bifurcated hydrogen bonds are intermolecular in nature. The hydrogen atom (H1A) of the coordinated water molecule (O1) forms bifurcated hydrogen bonds with the oxygen atoms (O3 and O5), while another hydrogen atom (H1B) of the uncoordinated water molecule (O7) forms bifurcated hydrogen bonds with carbonyl oxygen atoms (O9 and O10) of bpca. Such types of hydrogen bonds have already been investigated by earlier workers$^{22,23}$. The intermolecular $\pi$-$\pi$ stacking interaction is also present in complex (2). The distance between both centroids [Cg(I) to Cg(J)] is 3.584Å, while the dihedral angle is 0°. The angles and distances between centroids for complex (2) are listed in Table S2 (Supplementary Data).

Electron paramagnetic resonance (epr) studies

The epr spectra of both complexes, recorded in DMSO at 77 K, showed four well resolved hyperfine lines corresponding to coupling of the electron spin with the nuclear spin ($^{65,65}$Cu, $I = 3/2$) obtained in the parallel region (Fig. 4). In $g_{\perp}$ region nitrogen ($^{14}$N; $I = 1$) superhyperfine coupling ($A_1 = 170 \times 10^{-4}$ cm$^{-1}$) is reflected, which indicates an axially symmetric anisotropy with $g_{\perp}$ region showing multiple N-superhyperfine lines. The DMSO solution spectra
(at 77 K) of complexes (1) and (2) clearly axial (g\| > g⊥ > 2.0023) and suggested d_{x^2-y^2}^z^2 ground state for copper(II) in square based geometry. The broad epr signal at ~ 3450 G is clearer in complex (2) than in complex (1). The g\| values of the complexes are found to be less than 2.3 (Supplementary Data, Table S3) which indicate considerable covalent character of the M-L bond.

**Electronic and IR spectroscopy**

Visible spectra of these complexes have been recorded in 100% DMSO solution. Both complexes exhibit similar electronic spectra consisting of a broad d-d band at 700 nm for (1) and 653 nm for (2) (Supplementary Data, Fig. S1). The complex has a charge transfer band at 391 and 419 nm for (1) and (2) respectively. Presence of d-d band at 700 nm is expected for distorted square pyramidal geometry. The possibility of trigonal bipyramidal geometry at the metal center is ruled out because the pattern of λ_{max} > 800 nm along with the shoulder at ~660 nm was not observed in the case of the present complexes. The IR spectra of the complexes were recorded in KBr pellets. A broad band present at 3460 cm\(^{-1}\) and 3433 cm\(^{-1}\) in (1) and (2) indicates the presence of crystallization water molecule. In complex (1), a sharp medium band observed at 1618 cm\(^{-1}\) and 1710 cm\(^{-1}\) indicates the presence of –CONH\(_2\) group. In complex (2), a sharp medium intensity band arises at 1638 cm\(^{-1}\) due to –CO-NH- group while a medium intense band has observed at 1375 cm\(^{-1}\) due to ν(NO\(_3\)) in the ionosphere. The Cu-O bands were observed at 420 and 434 cm\(^{-1}\) along with Cu-N band at 492 cm\(^{-1}\) and 497 cm\(^{-1}\) for (1) and (2) respectively.

**DNA cleavage activity**

The complexes were tested for antibacterial activity against E. coli, Citrobacter and Vibrio sp. Both complexes showed lower activity than the standard antibiotic (Chloramphenicol) with complex (2) being more active than (1).

The interaction of copper(II) complexes (1) and (2) with pBR 322 DNA was monitored by observing the conversion of supercoiled (Form I, fastest migrating species) to open circular form (Form II). The activity of the complexes in effecting DNA cleavage was investigated by gel electrophoresis using pBR322 DNA in 5 mM Tris-HCl/50 mM NaCl buffer solution (pH 7.1). The metal complexes were able to convert supercoiled DNA into open circular DNA. The general oxidative mechanism and account of DNA cleavage by hydroxyl radicals via abstraction of a hydrogen atom from sugar units that predict the release of specific residues arising from transformed sugars, depends on the position from which the hydrogen atom is removed. The cleavage is inhibited by free radical scavengers implying that hydroxyl radical derivatives mediate the cleavage reaction. The reaction is modulated by a metallo-complexes bound hydroxyl radical generated from the co-reactant H\(_2\)O\(_2\). As can be seen from the results (Fig. 5), the complexes exhibit nuclease activity in the presence and absence of H\(_2\)O\(_2\). The requirement for a reductant for the cleavage of DNA by copper complexes suggests that Cu(II) ions are being reduced to Cu(I) ions, which are susceptible to subsequent oxidation by dioxygen in air. The resulting reactive oxygen species diffuses into the double standard DNA and cleaves it.

**Conclusions**

We have isolated two copper(II) complexes viz., [Cu(IDA)-(2-pa)]2H\(_2\)O (1) and [Cu(bpca)(H\(_2\)O)\(_2\)]NO\(_3\)·2H\(_2\)O (2) derived from tptz and characterized by various physicochemical techniques. Both complexes have a combination of coordination and hydrogen bonds. Complex (2) has bifurcated hydrogen bonds and \(\pi-\pi\) stacking interactions. In the present complexes, the trends g\| > g⊥ > 2.0023 is consistent with a \(d_{x^2-y^2}^z^2\) ground state in a square pyramidal geometry. These complexes showed antibacterial and DNA cleavage activity.

**Supplementary Data**

CCDC 859522 and 859523 contain the supplementary crystallographic data for [Cu(IDA)-(2-pa)]2H\(_2\)O (1) and [Cu(bpca)(H\(_2\)O)\(_2\)]NO\(_3\)·2H\(_2\)O.
These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or from the Director, CCDC, 12 Union Road, Cambridge, CB2, IEZ, UK, (Fax: +44 1223 336 033; Email: deposit@ccdc.cam.ac.uk). Other supplementary data associated with this article, i.e., Fig. S1 and Tables S1-S3, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_52A(06)717-723_SupplData.pdf.

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References